Diamond & Related Materials 75 (2017) 96–104

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

The composition, microstructure and mechanical properties of Ni/DLC nanocomposite films by filtered cathodic vacuum arc deposition

Han Zhou, Qingyan Hou, Tianqing Xiao, Yudong Wang, Bin Liao, Xu Zhang *

Beijing Normal University, Beijing Radiation Center, Beijing 100875, China

ARTICLE INFO

Article history:
Received 15 November 2016
Accepted 12 February 2017
Available online 14 February 2017

Keywords:
Nanocomposite films
Filtered arc deposition
CH_4 flow rate
C_2H_2 flow rate

ABSTRACT

In this paper, Ni/DLC nanocomposite films were deposited on the un-heated silicon (100) by the filtered cathodic vacuum arc deposition (FCVAD) under different CH_4 and C_2H_2 flow rates. The composition, microstructure and mechanical properties of the Ni/DLC films were investigated by scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and nanoindentation. The Ni/DLC films typically consisted of nickel nanograins around 11 nm, which were embedded in amorphous carbon matrix with the thickness of 0.35–2.8 nm. The film structure and the mechanical properties are strongly affected by the precursor gas type and flow rate. The porous structure, with the nanopore size equaling to the nickel grain size, can be seen after the etching process of the as-deposited film, providing a possible method for the preparation of nanoporous DLC films. A maximum hardness of 13.2 GPa and 21.64 GPa is achieved for the Ni/DLC films under the CH_4 flow rate of 30 sccm and C_2H_2 flow rate of 40 sccm, respectively, under which the maximum thickness of the amorphous carbon phase is also obtained.

1. Introduction

Metal containing carbon nanocomposite films (Me/DLC films) [1–6] which include metal or metal carbide phase embedded in amorphous carbon matrix have attracted a significant attention for the past few decades. The association between the carbon matrix and the encapsulated metallic or metal carbide phase not only improve the overall properties of the nanocomposite films [1,7,8], but also reduce the residual stress in the films which is always an obstacle for the preparation of high quality DLC films. As a transition metal, nickel has always been selected for the preparation of Me/DLC films because its catalysis on the DLC phase, which induces the graphitization of the amorphous carbon and the accompanying phase and structure changes, as well as the noticeable properties of the Ni/DLC films. The microstructure evolution and phase transition based on the deposition temperature, the radio of carbon and nickel content and other deposition parameters have been focused on the Ni/DLC films [2,3,9]. Accordingly, a series of properties such as the electromagnetism, thermostability, biocompatibility and thermistor have also been investigated [10–12].

To acquire the Me/DLC films, a series of method were carried out such as magnetron sputtering [5], microwave plasma-assisted chemical vapor deposition [11], co-sputtering [9,13], hyperthermal ion deposition [14], and cathodic arc deposition [15]. Comparing with other deposition techniques, filtered cathodic vacuum arc deposition (FCVAD) shows significant advantages such as the fast deposition rate, deriving the dense and ultra-hard films by filtering the large and neutral particles and controlling the composition of the films by conveniently adjusting the device parameters, which can be used more widely for industrialization [16]. During the plasma deposition process, expect for the experiment parameters mentioned above, the ion bombardment, which can be adjusted by tuning the bias voltage, arc voltage and the flow rate of precursor gas, also plays an important role on the microstructure and the phase transition of films by affecting the surface atom mobility and internal stresses, which have been highlighted in [16–18].

Therefore, this paper investigates the effect of CH_4 and C_2H_2 flow rate on the chemical composition, the structure evolution as well as the mechanical properties of the Ni/DLC nanocomposite films by the FCVAD method.

2. Experimental procedure

The nanocomposite Ni/DLC films were deposited on (100) single crystalline silicon wafers by filtered catholic vacuum arc system in a CH_4 and C_2H_2 atmosphere respectively. The schematic of the device is shown in Fig. 1. A 100 mm in diameter and a purity of 99.99% of Ni cathode was triggered to produce Ni plasma at a constant arc current of 100 A. The Ni plasma was then affected by an electromagnetic field and imported into the vacuum chamber through a 90° bent duct. The base pressure of deposition chamber was adjusted to $3 * 10^{-3}$ Pa before the experiment and the substrate bias was −200 V. During the experiment, the gas flow rate was 10, 20, 30 and 40 sccm, respectively. With increasing the gas flow rate, the chamber pressure increased steadily

* Corresponding author.
E-mail address: zhangxu@bnu.edu.cn (X. Zhang).

http://dx.doi.org/10.1016/j.diamond.2017.02.012
0925-9635/

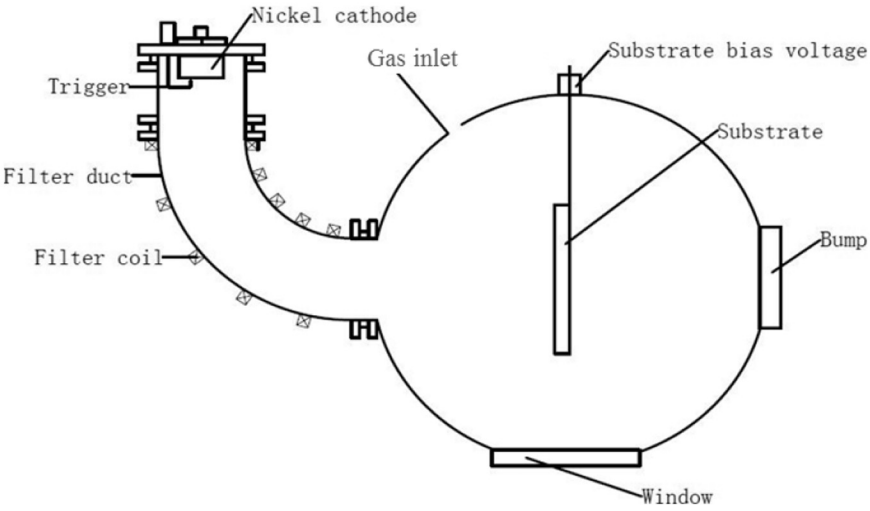

Fig. 1. Schematic diagram of filtered cathodic vacuum arc deposition system.

from $1.5 * 10^{-2}$ Pa at 10 sccm to a maximum of $4.8 * 10^{-2}$ Pa at 40 sccm and the deposition rate increased correspondingly.

The microstructure and chemical compositions of nc-Ni/DLC films were examined by Hitachi S-4800 Scanning Electron Microscope (SEM) and relevant EDS respectively. Grazing angle X-ray diffraction (GAXRD) measurement was selected for characterizing the crystal structure of the films, using Ringaku Dlmax 2500 diffract meter with Cu $K_{\alpha 1}$ radiation. The incident angle was 1°and the scanning range of 2θ was 10–90°. To obtain the average grain size, Scherrer's formula of $d = \frac{k\lambda}{B\cos\theta}$ was used, where k, B, λ, and θ are the constant of 0.89, full width at half maximum (FWHM) (°),wavelength (nm) and distraction angle (°), respectively. Raman spectra were acquired with a Jobin-Yvon HR800 monochromater cooled CCD at 7 mW power, and the 532 nm line of Ar-Kr laser was used. The surface chemical states of the films were investigated by X-ray photoelectron spectroscopy (XPS) using Al Kα radiation at 320 W constant powers. To exclude the contaminant on the surface of the films, the Ar^+ sputtering for 30 s was used on the films. The film thickness was measured by surface morphology instrument with the pattern of Talysurf 5P-120 and the deposition rate was measured accordingly. Nanohardness and modulus of elasticity were measured by Wrexham Micro Materials Ltd. Nano test system equipped with a Berkovich diamond tip applying a constant load of 2 mN and six indentations at different places on the surface were measured. To avoid the influence of the substrate, etch indentation depths were ranged from 5% to 10% of the film thickness.

Moreover, the etching process for the as-deposited films immersed in 3 M HCl solution for 24 h was employed for a better understanding of the structure composition of the Ni/DLC films. The etched films were rinsed by deionized water to exclude the residues in the films and then dried under 60 °C for 10 h.

3. Results and discussion

3.1. Composition

The compositions of the as-deposited Ni/DLC nanocomposite films under different CH_4 and C_2H_2 flow rates are shown in Fig. 2. With increasing the C_2H_2 flow rate, the carbon content in the Ni/DLC nanocomposite films increases from 19.5 at.% at 10 sccm to a maximum of 59.9 at.% at 40 sccm while the nickel content decreases from 80.5 at.% at

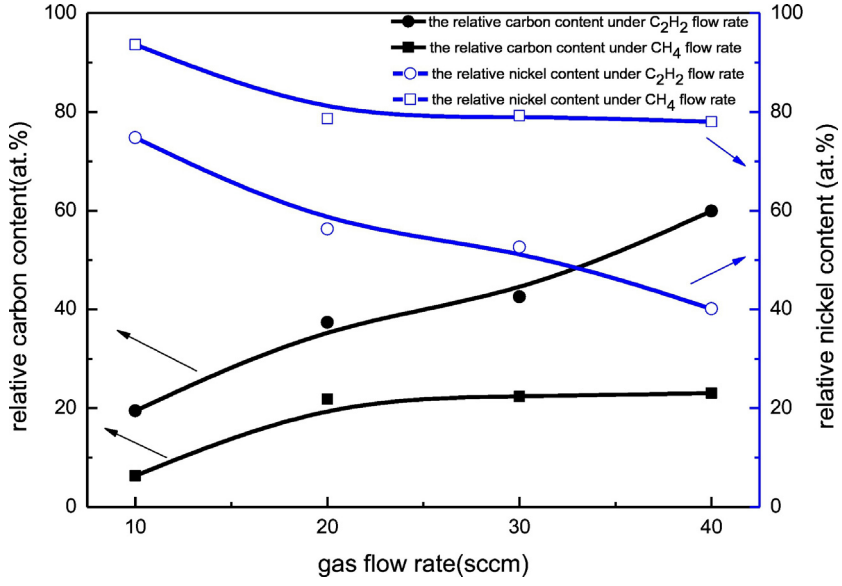

Fig. 2. The comparison of relative content of nickel and carbon in the films under different CH_4 and C_2H_2 flow rate respectively.